On the integration accuracy in molecular density functional theory calculations using Gaussian basis sets

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Abstract

The sensitivity of computed DFT (Density Functional Theory) molecular properties (including energetics, geometries, vibrational frequencies, and infrared intensities) to the radial and angular numerical integration grid meshes, as well as to the partitioning scheme, is discussed for a number of molecules using the Gaussian 98 program system. Problems with typical production grid sizes are particularly acute for third-row transition metal systems, but may still result in qualitatively incorrect results for a molecule as simple as CCH. Practical recommendations are made with respect to grid choices for the energy(+gradient) steps, as well as for the solution of the CPKS (Coupled Perturbed Kohn-Sham) equations.

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I. INTRODUCTION AND THEORETICAL BACKGROUND

Density Functional Theory (DFT) [1,2] has in recent years become both a powerful and a very commonly used tool for studying molecular electronic structure. In addition to usually reliable energetics, the availability of analytical first and second derivatives for the DFT approaches allows for easy calculation of geometric structure and vibrational frequencies.

The rate-determining step in molecular DFT calculations using Gaussian basis sets is usually the evaluation of various integrals over the exchange-correlation functional and its geometric derivatives. In practice the three-dimensional numerical integration is carried out as a weighted sum of three-dimensional integrations in polar coordinates centered on atoms A:

$$\int F(\mathbf{r})d\tau = \sum_A^{\text{atoms}} \sum_g^{\text{grid}} w_{gA} p_A(\mathbf{r_g}) F(\mathbf{r}_{gA}) \tag{1}$$

in which the $\mathbf{r}_g$ and w_g are numerical quadrature abscissae and weights, respectively, and the partitioning function p_A satisfies $\sum_A p_A(\mathbf{r}) = 1$ for all values of $\mathbf{r}$. In other words, p_A acts as a 'fader function' between grids centered on different atoms.

Quite separate from issues involving the basis set and mathematical form of the exchange-correlation functional, which determine the *accuracy* of the calculation, the choice of atomic integration grid and partitioning can have a profound impact on its numerical *precision* (together with trivial parameters like convergence criteria). Especially since an increasing proportion of users of quantum chemical software in general — and DFT methods in particular — are experimental chemists without prior background in electronic structure theory, the tendency exists to simply rely on the built-in defaults of various codes.

In the present paper, we shall report a number of problems which may arise in this fashion. Because of its great popularity and widespread use, our discussion will focus on the Gaussian 98 [3] program system. We wish to emphasize, however, that the issues raised in the present work could arise with other DFT codes. We note that some codes try to minimize possible numerical problems by the use of large default integration grids and/or by variation of the grid mesh with the atom type. While the use of very large grids certainly avoids

numerical problems, it can lead to prohibitively expensive calculations for larger systems. Therefore, it is of interest to find the smallest grid that will yield precise results for molecular properties.

Before proceeding to discuss our results, we shall first briefly review some relevant mathematical aspects.

II. MATHEMATICAL BACKGROUND

The atomic integration grid is built up naturally as the direct product of radial and angular grids:

$$\sum_g w_g F(\mathbf{r}_g) = \sum_a \sum_b w_a w_b F(r_a, \theta_b, \phi_b) \tag{2}$$

The angular grid itself can be either a direct product of appropriate one-dimensional Gauss quadrature grids (e.g., Gauss-Legendre or Gauss-Chebyshev), or (more efficiently) can be a two-dimensional Lebedev grid [4] which exactly integrates spherical harmonics up to a certain order. (In order to integrate spherical harmonics up to order L exactly, the direct product of grids with $(L+1)/2$ abscissae in θ and $L+1$ abscissae in ϕ requires $(L+1)^2/2$ angular quadrature points, compared to approximately $(L+1)^2/3$ for the corresponding Lebedev grid [5].)

The radial grids discussed in the present paper are all of the Murray-Handy-Laming (MHL) variety [6] (following ideas first proposed by Boys and Handy [7]), in which the infinite interval $r = [0, \infty]$ is remapped onto the finite interval $q = [0, 1]$ by means of the change of variable $r = \alpha(q/(1-q))^m$; the integration in q is then approximated by Euler-Maclaurin summation. (The latter is facilitated by the fact that $\left(\frac{d^n r}{dq^n}\right)$ vanishes at $q = 1$ for all n, and at $q = 0$ up to $n = 3m - 1$ inclusive.) Empirically, $m = 2$ is found to yield the best results [6], and α should be dependent on the atomic radius for best results. The following working equations arise for abscissae and weights:

$$r_i = R(i/(N + 1 - i))^2 \tag{3}$$

$$w_i = 2R^3(N + 1)i^5/(N + 1 - i)^7 \tag{4}$$

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in which N is the number of radial points and R is taken empirically [6] as one-half the Bragg radius of the atom on which the grid is centered (except for hydrogen, where R is set equal to the Bohr radius).

For molecular calculations, the partitioning function $p(\mathbf{r})$ introduced in Eq.(1) needs to be defined. One common choice is due to Becke [8]. Consider the confocal elliptical coordinate $\mu_{AB} = r_A - r_B/R_{AB}$ (in which r_A and r_B are distances towards nuclei A and B, and R_{AB} represents the internuclear distance), and define $p(\mu) = \frac{1}{2}[1 - g(\mu)]$, where $g(\mu)$ is the 'cell function'. The extreme choice $g(\mu_{AB})=-1$ if $\mu_{AB} \leq 0$; $=+1$ if $\mu_{AB} > 0$ (i.e. a Heaviside-type step function) would actually represent a scheme in which space is simply partitioned into Voronoi polyhedra: this will obviously be a numerically unstable scheme, since molecules by definition have appreciable electron density ρ (of which the integrand is a functional) near bond midpoints $\mu_{AB} = 0$. Becke [8] proposed to use a smoother approximation $g(\mu) = f(f(f(\mu)))$, where $f(\mu) = \frac{3}{2}\mu - \frac{1}{2}\mu^3$. Stratmann, Scuseria, and Frisch (SSF) [9] proposed to use a piecewise function instead, namely $g(\mu_{AB})=-1$ if $\mu_{AB} \leq -a$; $=+1$ if $\mu_{AB} \geq a$; $= \frac{1}{16}[35(\mu_{AB}/a) - 35(\mu_{AB}/a)^3 + 21(\mu_{AB}/a)^5 - 5(\mu_{AB}/a)^7]$ otherwise, where the scale factor $a = 0.64$ was determined empirically.[1] The SSF partitioning is reported to be numerically somewhat more stable, and in addition lends itself well to linear-scaling implementations [9].

III. COMPUTATIONAL METHODS

All calculations were carried out using Gaussian 98 Rev. A7 [3] running on various workstation computers at NASA Ames Research Center and the Weizmann Institute of Science.

A variety of Gaussian basis sets was used, including the Pople group 6-31G*, 6-31+G*,

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[1]As pointed out by a referee, this latter expression is equivalent to eq. (24), with $m=3$, of Ref. [6], although a piecewise $g(\mu)$ was not proposed there.

and 6-31++G** basis sets [10], the Dunning cc-pVDZ and cc-pVTZ basis sets (correlation consistent [11,12] polarized valence double and triple zeta, respectively), and the Hay-Wadt LANL2DZ (Los Alamos National Laboratory 2 Double-Zeta [13]) basis set-relativistic ECP combination.

In virtually all cases, the very popular B3LYP (Becke 3-parameter-Lee-Yang-Parr) hybrid exchange-correlation functional [14,15] was used, except for some test calculations using the earlier BLYP (Becke-Lee-Yang-Parr [15,16]) or BP86 (Becke-Perdew 1986 [16,17]) functionals.

We consider three types of grids:

- (nn,mmm), meaning the direct product of an nn-point Euler-Maclaurin radial grid with a two-dimensional Lebedev grid with mmm angular points;

- $(nn,mm,2mm)$, meaning the direct product of an Euler-Maclaurin grid with nn points in r and of Gauss-Legendre quadratures with mm and $2mm$ points in θ and ϕ, respectively;

- (nn,mmm)p, i.e. pruned (nn,mmm) grids. In pruned grids [18], the number of angular points is varied with the radial coordinate, with the full number of mmm only being used at r values relevant for conventional chemical bonding. In Gaussian 98, the following pruned grids are implemented: (35,110)p (invoked with the keyword "Grid=Coarse"), (50,194)p (the SG-1 grid [18] invoked with the keyword "Grid=SG1"), (75,302)p (invoked with the keyword "Grid=Fine"), and (99,590)p (invoked as "Grid=UltraFine"). Pruned grids are only implemented for elements up to and including krypton: for heavier elements, the corresponding unpruned grid is substituted. (We note that in the implementation in Gaussian 98, the cutoff radii between segments with different angular grid meshes are dependent on the row in the Periodic Table: this in effect does result in some grid quality adjustment with the atomic number.)

In frequency calculations using analytical second derivatives [19], Gaussian 98 permits

the use of different grids for the evaluation of the energy and gradient on the one hand, and for the solution of the CPKS (coupled perturbed Kohn-Sham) equations on the other hand. The defaults of the program correspond to "Int(Grid=Fine) CPHF(Grid=Coarse)"; specifying "Int(Grid=UltraFine)" implies "CPHF(Grid=SG1)" by default.[2]

Unless noted otherwise, tightened convergence criteria were used in geometry optimizations.

IV. RESULTS AND DISCUSSION

A. CCH radical

The acetyl radical is linear with a $^2\Sigma^+$ ground state. At the B3LYP/cc-pVTZ level with the default grid combination, however, one surprisingly finds (Table I) not only an imaginary bending frequency, but that the two "degenerate" components differ by 64 cm^{-1}. Upon repeating the calculation with an extremely large (140,48,96) grid, a properly degenerate bending frequency of 312.5 cm^{-1} (intensity 3.84 km/mol) was found, irrespective of whether Becke or SSF partitioning is used. Taking the SSF (140,48,96) result as the reference, we find the default grid to be in error by only 0.3 and 0.1 cm^{-1} for the CC and CH stretches, respectively, while the two components of the bending frequency are off by a whopping -421 and -492 cm^{-1}, respectively. (N.b.: we have treated the imaginary frequencies as negative numbers when we compute the error.) Likewise, while errors of about 5 and 1 % are seen for the CC and CH intensities, respectively, the bend intensity is too high by an order of magnitude. Using Becke instead of SSF weights does not materially affect these observations.

Specifying "Grid=Ultrafine" (i.e. (99,590)p for integration, and (50,194)p for CPKS) leads to a dramatic improvement in the bending frequency, which is now properly degener-

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[2]In Gaussian 98, the keyword CPHF controls options for both the Coupled Perturbed Hartree-Fock procedure in wavefunction based ab initio calculations and for CPKS in density functional calculations.

ate and only 7 cm^{-1} too low. (The intensities for the other two modes now agree with the reference values to two decimal places.) The error in the corresponding infrared intensity drops by two orders of magnitude. Specifying the (99,590)p grid for both integration and CPKS does not affect the stretching frequencies, but reduces the error on the bending frequency and intensity to 0.1 cm^{-1} and 0.01 km/mol, respectively, using either Becke or SSF partitioning. This clearly suggests that sensitivity is greatest to the CPKS grid.

Using the (75,302)p grid for integration and varying the CPKS grid from the associated (35,110)p default, we find that the spurious imaginary, nondegenerate bending frequencies disappear upon using either the unpruned (35,110) or the larger pruned (50,194)p grid. However, errors of about –10 and –7 cm^{-1} in the bending frequency remain, and are not reduced to the 1 cm^{-1} range until a (75,302)p or even (75,302) CPKS grid is substituted. Upgrading the energy grid to (99,590)p does not affect these conclusions.

Surprisingly, using a (99,974) grid for both integration and CPKS yields slightly different frequencies for the two components of the π bending mode.

Upon finding an imaginary frequency, one is tempted to displace the molecular geometry in the direction of that mode and reoptimize the geometry. Following this procedure, using the Gaussian 98 defaults (an energy grid of (75,302)p, a CPKS grid of (35,110)p, and the SSF weights), one obtains a HCC angle of 171.1 degrees and three real frequencies. However, one of the six trivial vibrations (i.e., overall translation and rotation, which should have exactly vanishing frequencies in an infinitely precise calculation using a rotationally invariant method) has a frequency of 508i cm^{-1}. Thus lowering symmetry has just made the numerical problem less obvious.

Unlike the frequencies which show a large sensitivity to the choice of grid, the total energy of CCH is in error by less than 1 microhartree for all grids studied. Considering the small effect on the energy, it is not surprising that the CCH results are most sensitive to the CPKS grid.

B. Harmonic frequencies of TaCl$_2$

The ground state for this symmetric linear molecule is X $^4\Sigma_g^-$. Results at the B3LYP/LANL2DZ level as a function of the integration and CPKS grids are summarized in Table II. Our largest grid (140,48,96) SSF results will again be considered as the reference.

None of the grid combinations considered in Table II lead to nonequivalent bending vibration components, but the default grid combination does produce a spurious imaginary bending frequency. Unlike CCH, the bending infrared intensities agree well with the largest grid value, but the symmetric and antisymmetric stretching frequencies are in error by -6 and -7 cm^{-1}, respectively. Use of the Becke partitioning leads not only to increased errors in the stretching frequencies, but to an error of $+0.002$ Å in the optimum bond distance, compared to -0.0003 Å with the SSF partitioning. Quite different from the behavior for CCH is the fact that the total energy is now in error by 310 microhartree with the SSF partitioning, and 369 microhartree with the Becke partitioning.

In this particular case, varying the size of the CPKS grid, and particularly of its angular component, does not appear to remedy the problem at hand. Using an unpruned energy grid, however[3], or using a grid with more radial points, dramatically reduces the error in the computed total energy, bond distance, and frequencies, particularly using the SSF partitioning. In particular, the (99,590)p/(50,194)p integration/CPKS grid combination invoked by "Grid=UltraFine" incurs (with SSF partitioning) no error greater than 1 cm^{-1} on the frequencies, and reduces the errors in bond distance and total energy to 0.0001 Å and 1.5 microhartree, respectively. While it is possible that using the Becke atomic size adjustment procedure (Appendix of Ref. [8]), in conjuction with the SSF weights, would reduce the sensitivity to the radial grid, we note that using the 'UltraFine' grid combination solves both the CCH angular grid problem and the TaCl$_2$ radial grid problem, and therefore would seem

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[3] Note that this change will only affect the Cl atomic grid in this case, as grids for elements heavier than Kr are always unpruned in Gaussian 98.

to be a good choice to invesigate possible grid problems.

For TaCl$_2$, performance of the SSF partitioning seems markedly superior to that of the Becke partitioning. As expected, differences between the two partitioning schemes are reduced as the grid is improved, and they yield essentially identical results for the (140,48,96) grid.

Lowering the symmetry to C_{2v} and using the Gaussian 98 defaults results in a slightly bent structure with a ClTaCl angle of 171.1 degrees. As in the case of CCH, the only indication of the numerical problems is in the deviation from zero of the translational and rotational frequencies, but for TaCl$_2$ the value is $33i$ cm^{-1}, making the error for TaCl$_2$ less obvious than in the case of CCH (see above).

If we now consider relative CPU times (default grids=1.00) as a function of grid size, we see that the (99,590)p/(50,194)p combination will approximately double CPU time. Using a (99,590)p grid for both integration and CPKS is found to be a factor of nine more expensive than the default, a ratio which goes up to a factor of 19 for the unpruned (99,974) grid, of 36 for the (96,32,64) grid often cited in benchmarks, and of 109 for the largest (140,48,96) grid considered here. The (99,590)p/(75,302)p combination found to be required for 1 cm^{-1} precision in the bending frequency of CCH would be four times more expensive than the default — rather more time-consuming than desirable, but still an order of magnitude less expensive than the (96,32,64) grid.

C. Harmonic frequencies of Ge$_2$H$_5$ and Ge$_2$H$_6$

Ge$_2$H$_6$ has D_{3d} symmetry and a structure analogous to ethane. Ge$_2$H$_5$ is best viewed as removing one H from Ge$_2$H$_6$, which results in C_s symmetry; there is only a small change in the structural parameters relative to the parent Ge$_2$H$_6$ molecule.

In Table III we summarize our results for Ge$_2$H$_5$. In addition to the effect of partitioning and grid size, we also consider the influence of the basis set and of the exchange-correlation functional on the three lowest harmonic frequencies of Ge$_2$H$_5$. We first consider using the Becke partitioning. Using the default grid in Gaussian, i.e. a pruned (75,302)p grid for energy

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and gradients and (35,110)p for CPKS, results in an imaginary frequency. Expanding the radial grid from 75 to 96 points and depruning the grid, i.e. the (96,302) grid, for the energy, gradient, and CPKS steps does not remove the imaginary frequency. Expanding the angular grid removes the numerical problem; with 590 angular points, the lowest harmonic frequency is essentially converged to a value of about 100 cm^{-1}. Expanding the radial grid further has only an effect of a few cm^{-1}.

The results using SSF partitioning are very different from those obtained using Becke partitioning; using SSF, even the default "Grid=Fine" is precise to better than 10 cm^{-1}. Improving the grid makes much smaller changes for SSF and the "UltraFine" grid in Gaussian 98 (i.e., (99,590)p for energy and gradients, (50,194)p for CPKS) appears to be essentially converged. Note that for the Becke partitioning the "UltraFine" grid also yields essentially converged results.

Adding diffuse functions to the Ge atoms or diffuse and polarization functions to the H atoms does not eliminate the imaginary frequency for the default grid and the Becke partitioning. That is, the problem is not unique to the 6-31G* basis set.

Nor is it unique to the use of a hybrid functional: substituting the BP86 functional for its B3LYP counterpart does not alter the trends with respect to partitioning and grid, the most notable point being the imaginary frequency for the default grid with Becke partitioning.

The Ge_2H_5 calculations are repeated using the LANL2DZ basis set/ECP combination, and the results are also given in Table III. Unlike the all-electron calculations, there is essentially no difference between Becke and SSF partitioning, and improving the grid has only a very small effect. This is also true for the four- and 14-valence electron Ge ECPs of Hurley *et al.* [20]. Thus it appears that the difference observed in the all-electron calculations arises from the inner-shell orbitals.

For the default grids and the Becke partitioning, displacing the molecular geometry in the direction of the imaginary mode results in essentially the same geometry and frequencies as found in the C_s treatment. That is, lowering the symmetry does not eliminate the imaginary frequency, so the numerical problems are much more obvious than for CCH and $TaCl_2$.

Substituting Si for Ge leads to a similar structure, but as shown in Table IV, neither the choice of grid points nor the partitioning scheme make much of a difference for the Si_2H_5 system. The lack of sensitivity of the results to grid or partitioning is similar to the results reported [9] by SSF, and is typical of many other tests that we have performed for systems containing first and second row atoms. The problem of the imaginary frequency does not exist for Ga_2Cl_5: the Becke and SSF partitioning agree to within 4 cm^{-1} for the 6-31+G* basis set and the default grids. Given that Si_2H_5, Ge_2Cl_5, and Ge_2H_5 have similar shapes, we conclude that the shape of Ge_2H_5 does not lead to the numerical problems that result in the imaginary frequency.

In Table V we summarize the results for Ge_2H_6, which is a closed-shell, stable molecule. It shows the same variation in the frequencies with choice of partitioning and grid points as Ge_2H_5, and we conclude that the difference between results using Becke and SSF partitioning is not unique to Ge_2H_5. It is encouraging that the default SSF partitioning is less sensitive to the choice of grid, but it is also sobering to realize that it is possible to have an error of about 70 cm^{-1} with no obvious indication of an error.

D. Relative energies of cis- and trans-HIr[PR$_3$]$_4$Cl$^+$

The peculiar cis-trans equilibrium of the $HIr[PR_3]_4Cl^+$ (R=H, CH$_3$) transition metal complexes was the subject of a very recent joint theoretical-experimental investigation [21]. At the highest level of theory for R=CH$_3$, the complexes are found to be essentially isoenergetic, with the equilibrium between the two being essentially wholly driven by the higher entropy of the cis form: experimentally [21], a 6:1 cis:trans equilibrium is found at room temperature.

Given the very small energy differences being considered here, as well as the rather flat potential surface of particularly the cis form, grid convergence (not discussed in Ref. [21]) was obviously a cause for concern here. Upon first optimizing the cis-R=CH$_3$ case using the default grids and computing vibrational frequencies, we found what appeared to be a local minimum. Upon recomputing the harmonic frequencies with the (99,590)p/(50,194)p

integral/CPKS grid combination, we found this structure to be a saddle point of order 3, and only after thirteen geometry optimization cycles using analytical second derivatives (and two months of CPU time on an SGI Origin 2000) was the true minimum structure found. A superimposition of the two structures (created using the MOLDEN [22] molecular viewing program) is displayed in Figure 1.

While the R=CH$_3$ case is simply too large to do an exhaustive grid convergence study, we have summarized some data for the R=H case in Table VI. In particular, we have considered the absolute energies for the cis and trans isomers, and their relative energy, as a function of grid size. In this case, results seems to be quite dependent both on the radial and on the angular grid mesh. Using the (35,110)p grid employed by default in the CPKS step, the relative energy gets predicted with the wrong sign, and neither the use of an unpruned grid nor switching to a product grid of the same order remedy the problem — if anything, results get *worse*, suggesting that the (35,110)p results in fact benefit from a fortunate error compensation. Total energies are off by as much as 8 *milli*hartree for the trans isomer. While a scatter in the energies does not necessarily imply a corresponding scatter in the CPKS solution, it does not seem entiely implausible that a grid that predicts isomer energy differences on a surface with the wrong sign might yield a Hessian with incorrect curvature if used in the CPKS step.

The smallest grid that at least predicts the correct sign for the cis-trans difference is (50,194)p (about 25% too high in absolute value): using an unpruned grid instead[4] cuts the error in half, as does using the (75,302)p grid. Total energies are however still in error by amounts of about 60 microhartree: fortunately the errors largely cancel. The (99,590)p ("UltraFine") grid agrees to two decimal places with the (140,48,96) reference results; even a grid as large as (99,974) cannot yet achieve 1 microhartree precision in the total energies, which is barely reached for a (99,27,54) grid, and more comfortably for a (99,32,64) grid.

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[4] Again, since the Ir grid is always unpruned, the improvement in grid quality comes from additional grid points centered on the other atoms.

V. CONCLUSIONS

Computed molecular properties using density functional theory in general, and vibrational frequencies in particular, tend to be quite sensitive to the integration grids and partitioning being used in the calculation. Our results corroborate the assertion of SSF that their proposed partitioning scheme is numerically more stable than the Becke partitioning.

While the use of coarse grids in the solution of the CPKS (coupled perturbed Kohn-Sham) equations certainly leads to significant speedups, it can cause spurious negative eigenvalues in the Hessian matrix, or even artifactual loss of vibrational mode degeneracy, in systems as small and uncomplicated as CCH radical. While this problem is alleviated by the use of unpruned grids, this offers no benefit (in terms of CPU time) over the use of a larger pruned grid. For systems involving very heavy elements (e.g. third-row transition metals), grids which are sufficiently fine-meshed for typical first-and second-row systems are no longer adequate. In situations where small pruned grids are inadequate, the use of the corresponding unpruned grid appears to be less efficient than the use of a larger pruned grid.

For the cases considered here, the most efficient grid combination that appears to be 'immune' to qualitatively incorrect results is (99,590)p for energy and gradients, (50,194)p for CPKS. (This is equivalent to the "Grid=UltraFine" option in Gaussian 98.) For greater quantitative precision, the use of a finer-meshed (75,302)p grid for the CPKS is recommended. While a (99,974), (96,32,64) or even finer grid in all steps of the calculation will certainly avoid this type of problems, this comes at an unacceptably high premium in terms of CPU time.

As quantum chemical methods mature and quantum chemical software becomes more user-friendly, an increasing proportion of their users are scientists from other fields than quantum chemistry, who are inevitably exposed to the temptation to treat such program systems as 'black boxes'. Observations such as those made in the present paper illustrate that even at the present state of technology, 'black box' performance should not be taken for granted, and that acquiring some insight in both the quantum mechanical and numer-

ical methodology is still an essential prerequisite for their effective and reliable scientific application.

NOTE ADDED

After acceptance of the present manuscript, and in response to a preprint thereof, we received a personal communication from Gary W. Trucks and Michael J. Frisch of Gaussian, Inc., informing us of a bug in Gaussian 98 which affects the integral (derivative) accuracy for the *specific* case of the (35,110)p grid. A fix will be incorporated in the next minor release after Rev.A9. The main effect on the data presented in this paper is that the errors in the first two entries in Table 1 become a good deal less dramatic: in particular, the degeneracy of the bend is restored and the errors in ω_3 and I_3 are reduced to -19 cm^{-1} and 1.2 km/mol, respectively. In addition, we reoptimized the complex in Figure 1 using a patched version of the code with the default grid combination (and using analytical second derivatives as before). The resulting geometry is in much closer agreement with the Grid=UltraFine structure. (The cis-trans difference with the (35,110)p grid in Table VI is not affected materially.) The authors would like to thank Drs. Trucks and Frisch for helpful discussions.

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TABLE I. Numerical errors in computed B3LYP/cc-pVTZ properties for acetyl radical as a function of grid size. The values are given for the largest grid, which is used as our reference.

Energy grid	CPKS grid	Partition scheme	$\Delta E(uEh)$ μE_h	$\Delta\omega_{3x}$ cm^{-1}	ΔI_{3x} km/mol	$\Delta\omega_{3y}$ cm^{-1}	ΔI_{3y} km/mol	$\Delta\omega_2$ cm^{-1}	ΔI_2 km/mol	$\Delta\omega_1$ cm^{-1}	ΔI_1 km/mol
(75,302)p	(35,110)p	B	0.65	-481.35	38.53	-417.12	30.42	-0.21	0.28	0.62	-0.53
(75,302)p	(35,110)p	SSF	-0.10	-492.09	39.55	-420.61	30.92	0.29	0.28	0.08	-0.55
(75,302)p	(35,110)	B	0.65	-10.07	0.61	-10.07	0.61	-0.32	0.00	0.44	0.00
(75,302)p	(35,110)	SSF	-0.10	-9.42	0.61	-9.42	0.61	0.17	0.00	-0.12	-0.01
(75,302)	(35,110)	B	0.59	-9.84	0.61	-9.84	0.61	-0.32	-0.01	0.45	0.00
(75,302)	(35,110)	SSF	-0.16	-9.25	0.61	-9.25	0.61	0.17	0.00	-0.11	0.00
(75,302)p	(50,194)p	B	0.65	-7.43	0.44	-7.43	0.44	-0.32	-0.01	0.44	0.00
(75,302)p	(50,194)p	SSF	-0.10	-6.79	0.44	-6.79	0.44	0.17	0.00	-0.12	-0.01
(75,302)p	(75,302)p	B	0.65	0.73	-0.08	0.73	-0.08	-0.32	-0.01	0.44	0.00
(75,302)p	(75,302)p	SSF	-0.10	1.34	-0.08	1.34	-0.08	0.17	0.00	-0.12	-0.01
(75,302)	(75,302)	B	0.59	0.08	-0.02	0.08	-0.02	-0.32	0.00	0.45	0.00
(75,302)	(75,302)	SSF	-0.16	0.64	-0.02	0.64	-0.02	0.17	0.00	-0.11	0.00
(99,590)p	(50,194)p	B	-0.04	-7.06	0.45	-7.06	0.45	0.06	0.00	0.10	0.00
(99,590)p	(50,194)p	SSF	0.12	-7.06	0.45	-7.06	0.45	-0.09	0.00	-0.29	0.00
(99,590)p	(75,302)p	B	-0.04	1.08	-0.07	1.08	-0.07	0.06	0.00	0.10	0.00
(99,590)p	(75,302)p	SSF	0.12	1.09	-0.07	1.09	-0.07	-0.09	0.00	-0.29	0.00
(99,590)p	(99,590)p	B	-0.04	0.11	-0.01	0.11	-0.01	0.06	0.00	0.10	0.00
(99,590)p	(99,590)p	SSF	0.12	0.12	-0.01	0.12	-0.01	-0.09	0.00	-0.29	0.00
(99,590)	(99,590)	B	-0.04	0.07	-0.01	0.07	-0.01	0.06	0.00	0.10	0.00
(99,590)	(99,590)	SSF	0.12	0.07	-0.01	0.07	-0.01	-0.09	0.00	-0.29	0.00
(99,974)	(99,974)	B	-0.06	0.01	0.00	0.73	0.00	0.06	0.00	0.08	0.00
(99,974)	(99,974)	SSF	0.11	0.03	0.00	0.73	0.00	-0.08	0.00	-0.25	0.00
(99,36,72)	(99,36,72)	B	-0.07	0.14	-0.01	0.14	-0.01	0.06	0.00	0.08	0.00
(99,36,72)	(99,36,72)	SSF	0.11	0.15	-0.01	0.15	-0.01	-0.08	0.00	-0.25	0.00
(140,48,96)	(140,48,96)	B	0.00	0.01	0.00	0.01	0.00	0.02	0.00	-0.01	0.00
(140,48,96)	(140,48,96)	SSF	...[a]	312.54	3.85	312.54	3.85	2094.63	5.05	3456.85	56.60

[a] The total energy is -76.63761769 Hartrees.

TABLE II. Numerical errors in computed B3LYP/LANL2DZ properties of TaCl$_2$ (X $^4\Sigma_g^-$ state) as a function of grid size. The values are given for the largest grid, which is used as our reference.

Energy Grid	CPKS Grid	Partition scheme	Δr mÅ	ΔE μE_h	$\Delta\omega_3$ cm^{-1}	ΔI_3 km/mol	$\Delta\omega_2$ cm^{-1}	$\Delta\omega_1$ cm^{-1}	ΔI_1 km/mol	relative CPU time
(75,302)p	(35,110)p	B	1.86	368.55	-60.21	0.02	-7.67	-8.86	-0.23	1.00
(75,302)p	(35,110)p	SSF	-0.26	309.60	-59.90	-0.01	-5.40	-6.80	-0.01	1.00
(75,302)	(35,110)	B	0.04	-17.03	3.97	0.00	0.15	0.20	-0.01	3.05
(75,302)	(35,110)	SSF	0.11	-5.48	1.83	0.00	-0.15	-0.16	-0.01	2.98
(75,302)p	(50,194)p	B	1.86	368.55	-60.25	0.02	-7.67	-8.85	-0.22	2.02
(75,302)p	(50,194)p	SSF	-0.26	309.60	-59.95	-0.01	-5.40	-6.80	0.00	2.01
(75,302)p	(75,302)p	B	1.86	368.55	-60.26	0.02	-7.67	-8.86	-0.22	3.86
(75,302)p	(75,302)p	SSF	-0.26	309.60	-59.95	-0.01	-5.41	-6.80	0.00	3.82
(99,590)p	(35,110)p	B	0.09	-16.84	4.52	0.00	0.15	0.23	-0.02	1.16
(99,590)p	(35,110)p	SSF	0.10	-1.54	0.91	0.00	-0.06	-0.04	-0.02	1.15
(99,590)p	(50,194)p	B	0.09	-16.84	4.49	0.00	0.15	0.23	-0.01	2.19
(99,590)p	(50,194)p	SSF	0.10	-1.54	0.88	0.00	-0.06	-0.04	-0.01	2.17
(99,590)p	(75,302)p	B	0.09	-16.84	4.49	0.00	0.15	0.23	-0.01	4.00
(99,590)p	(75,302)p	SSF	0.10	-1.54	0.88	0.00	-0.06	-0.04	-0.01	3.97
(99,590)p	(99,590)p	B	0.09	-16.84	4.49	0.00	0.15	0.23	-0.01	8.96
(99,590)p	(99,590)p	SSF	0.10	-1.54	0.88	0.00	-0.06	-0.04	-0.01	8.91
(99,974)	(99,974)	B	0.00	0.11	-0.02	0.00	-0.01	-0.01	0.00	19.2
(99,974)	(99,974)	SSF	0.00	0.14	0.00	0.00	-0.01	-0.02	0.00	19.1
(96,32,64)	(96,32,64)	B	0.00	-0.01	0.11	0.00	-0.02	-0.03	0.00	36.7
(96,32,64)	(96,32,64)	SSF	0.00	0.28	0.00	0.00	-0.05	-0.06	0.00	36.3
(99,48,96)	(99,48,96)	B	0.00	0.08	0.00	0.00	-0.01	-0.01	0.00	80.1
(99,48,96)	(99,48,96)	SSF	0.00	0.14	0.00	0.00	-0.01	-0.02	0.00	79.1
(140,48,96)	(140,48,96)	B	0.00	0.00	0.01	0.00	0.00	0.00	0.00	110.4
(140,48,96)	(140,48,96)	SSF	2335.357	...^{a}	35.89	3.96	347.51	375.63	107.73	109.4

^{a} The total energy is –87.74246174 Hartrees.

TABLE III. Summary of the three lowest harmonic frequencies of Ge_2H_5.

Energy Grid	CPKS Grid	Becke partitioning			SSF partitioning		
		B3LYP/6-31G*					
(75,302)p	(35,110)p	77.9i	250.2	352.2	114.2	250.5	363.6
(75,302)	(75,302)	77.6i	250.2	352.2	114.2	250.5	363.6
(96,302)	(96,302)	39.6i	250.2	356.0	101.0	250.4	361.5
(75,434)	(75,434)	44.6	250.4	365.5	107.4	250.4	358.4
(75,590)	(75,590)	108.4	250.3	360.6	95.3	250.4	360.4
(99,590)p	(50,194)p	106.4	250.4	359.9	103.1	250.4	360.0
(99,590)	(99,590)	106.5	250.4	359.9	103.1	250.4	359.9
(75,770)	(75,770)	103.6	250.3	360.5	105.8	250.4	361.5
(75,974)	(75,974)	107.7	250.3	360.2	103.9	250.4	360.5
(96,974)	(96,974)	106.2	250.3	360.5	105.0	250.4	360.3
(128,974)	(128,974)	106.8	250.4	360.3	105.2	250.4	360.1
		B3LYP/6-31+G*					
(75,302)p	(35,110)p	82.7i	250.7	352.8	111.6	250.8	364.1
		B3LYP/6-31++G**					
(75,302)p	(35,110)p	36.6i	252.8	349.7	110.9	252.8	368.8
		BP86/6-31G*					
(75,302)p	(35,110)p	109.8i	247.4	337.7	95.4	247.9	349.1
(99,590)	(99,590)	108.0	247.9	347.5	96.9	247.9	346.9
		B3LYP/LANL2DZ					
(75,302)p	(35,110)p	88.8	241.5	373.7	89.1	241.5	373.7
(99,590)	(99,590)	88.3	241.5	373.8	88.3	241.5	373.8

TABLE IV.   Summary of the three lowest and the three highest harmonic frequencies of Si_2H_5 using the 6-31G* basis set and the B3LYP functional.

Energy Grid	CPKS Grid	Partition Scheme	Harmonic frequencies					
(75,302)p	(35,110)p	B	123.4	390.4	407.1	2233.2	2244.8	2254.5
(75,302)p	(35,110)p	SSF	124.0	390.2	407.2	2227.9	2241.1	2250.8
(75,302)	(75,302)	B	123.3	390.4	407.0	2233.2	2244.8	2254.5
(75,302)	(75,302)	SSF	123.9	390.3	407.1	2227.9	2241.1	2250.8
(96,974)	(96,974)	B	122.2	390.6	408.6	2231.2	2243.5	2253.2
(96,974)	(96,974)	SSF	122.1	390.6	408.8	2229.9	2242.8	2252.4
(99,590)p	(50,194)p	B	125.4	391.2	409.8	2231.1	2243.3	2253.0
(99,590)p	(50,194)p	SSF	123.1	390.7	409.0	2230.8	2243.2	2252.8

TABLE V. Summary of the three lowest harmonic frequencies of Ge_2H_6 using the 6-31G* basis set and the B3LYP functional.

Energy Grid	CPKS Grid	Becke partitioning			SSF partitioning		
(75,302)p	(35,110)p	57.1	259.7	347.0	123.9	259.8	360.7
(75,302)	(75,302)	54.1	259.7	346.8	122.6	259.8	360.5
(75,434)	(75,434)	44.6i	259.7	351.7	116.8	259.8	353.0
(75,590)	(75,590)	93.0	259.7	347.5	111.7	259.8	356.3
(99,590)p	(50,194)p	94.2	259.8	347.3	107.7	259.8	353.2
(99,590)	(99,590)	94.5	259.8	347.3	107.9	259.8	353.2
(75,770)	(75,770)	106.6	259.7	353.9	112.3	259.8	355.1
(75,974)	(75,974)	110.7	259.7	353.6	108.6	259.8	354.1
(96,302)	(96,302)	75.2	259.7	351.9	109.9	259.8	356.3
(96,434)	(96,434)	30.0i	259.8	351.8	102.6	259.8	352.9
(96,974)	(96,974)	110.1	259.7	353.8	109.0	259.8	353.8
(128,974)	(128,974)	110.3	259.8	353.8	109.4	259.8	353.7

TABLE VI. Numerical errors in absolute and relative B3LYP/LANL2DZ energies of cis and trans isomers[a] of $HIr(PH_3)_4Cl^+$ as a function of grid size

Grid	ΔE trans(C_{4v}) μE_h	ΔE cis(C_s) μE_h	Isomerization energy kcal/mol
(35,110)p	2488.42	890.21	0.409
(35,110)	5638.22	1301.61	2.127
(35,9,18)	8400.38	113.28	4.606
(50,194)p	-236.21	112.62	-0.813
(50,194)	-118.27	17.55	-0.679
(50,12,24)	653.35	77.73	-0.233
(50,302)	-110.06	17.55	-0.674
(50,15,30)	-118.27	-95.50	-0.608
(75,302)p	-58.35	63.27	-0.670
(75,302)	-33.64	12.74	-0.623
(75, 15, 30)	-23.58	-44.17	-0.581
(99,194)	-68.07	52.53	-0.670
(99,12,24)	708.68	135.89	-0.235
(99, 302)	-33.52	10.52	-0.622
(99, 15, 30)	-21.44	-44.17	-0.580
(99, 590)p	-15.29	-7.81	-0.599
(99, 590)	-10.22	-5.75	-0.597
(99, 21, 42)	0.68	5.52	-0.597
(99, 974)	-2.29	0.70	-0.596
(99, 27, 54)	0.39	-0.97	-0.593
(99, 32, 64)	0.64	0.21	-0.594
(99, 36, 72)	0.11	0.13	-0.594
(50, 48, 96)	-85.20	-45.60	-0.619
(75, 48, 96)	-2.03	2.24	-0.597
(99, 48, 96)	-0.13	0.14	-0.594
(140, 48, 96)	0.00[b]	0.00[b]	-0.594
(50, 590)	-92.82	-49.43	-0.621
(75, 590)	-12.14	-3.19	-0.600
(99, 590)	-10.22	-5.75	-0.597
(120, 590)	-10.19	-5.89	-0.597

[a] Reference geometries were obtained at the B3LYP/LANL2DZ level with the (99,590)p/(50,194)p grid combination and tightened optimization criteria.

[b] Total energies: cis -153.25208234, trans -153.25302915 hartree.

FIG. 1. Superimposition of B3LYP/LANL2DZ optimized structures for cis-HIr[P(CH$_3$)$_3$]$_4$Cl$^+$
with the (75,302)p/(35,110)p (dark grey) and (99,590)p/(50,194)p (light grey) grid combinations.